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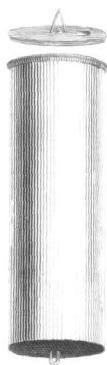
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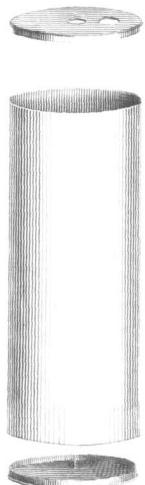
*Fig. 2.*



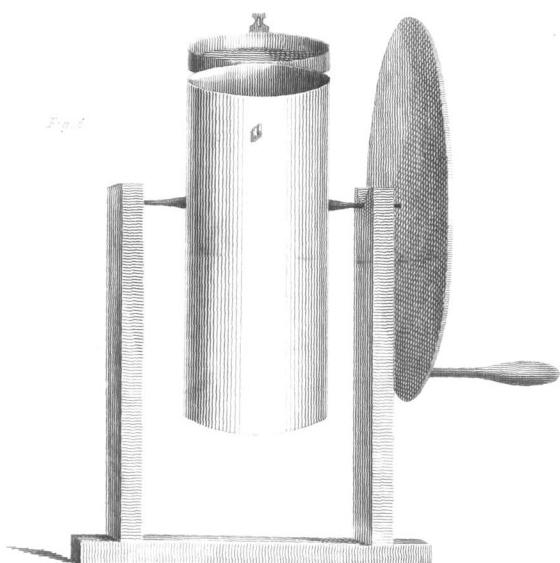
*Fig. 4.*



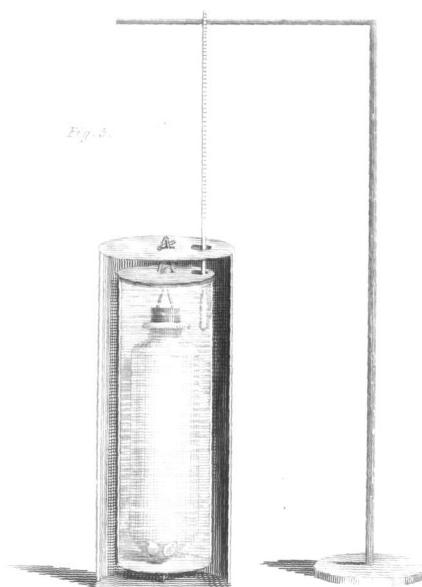
*Fig. 3.*



*Fig. 2.*



*Fig. 3.*



XVI. *On the Heat developed during the Formation of the Metallic Compounds of Chlorine, Bromine, and Iodine.* By THOMAS ANDREWS, M. D., M. R. I. A., Professor of Chemistry in the Royal Belfast Institution.

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Read December 12, 1842.

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1. IN pursuance of the train of investigation commenced in a preceding Memoir, I propose, in the present communication, to advance to the consideration of the more complicated thermal phenomena, which are accompanied by alterations in the state of aggregation of the combining bodies. To deduce general conclusions from such inquiries is extremely difficult, as the variation of temperature measured by the thermometer is in every instance the resultant of more than a single cause, each of which must be separately eliminated, before the heat arising from the chemical union can be determined. It has been my endeavour to furnish as many data as possible, in the cases I have examined, for the solution of these interesting problems.

2. That we may be enabled to measure with precision the heat developed during a chemical combination, it is necessary that the reaction should be very quickly completed; and the experiment is also greatly facilitated, when the action commences, by simple contact, without the application of external heat. These conditions are completely fulfilled, when chlorine, bromine, or iodine are brought into contact with zinc or iron, water being also present. To the success of the experiment the latter condition is indispensable, as these elementary bodies, at ordinary temperatures, and in the dry state, have no action upon one another.\*

\* The description generally given in chemical works of the rapid manner in which zinc, copper, antimony, &c. enter into combination with chlorine gas at common temperatures, is only true when the gas is in a moist state. Chlorine gas, when carefully dried, has no action whatever, at the ordinary temperature of the atmosphere, upon fine filings of zinc or iron, or upon copper reduced from

The relative proportion of water is also a matter of importance. The quantity present must be sufficient to dissolve, with facility, the resulting compound, and it ought not greatly to exceed that amount. In the following experiments I usually employed about 2.4 gr. of water, for every 0.42 gr. chlorine, 0.9 gr. bromine, and 1.5 gr. iodine, which entered into combination. If this precaution be attended to, and the mixture briskly agitated, the whole reaction will be completed in the course of a few seconds.

3. As our object is to ascertain the heat due to the combination of the reacting bodies in an anhydrous state, and as we actually obtain the result of the combination in a state of solution in water, it is obviously necessary, in the first instance, to apply a correction for the heat arising from the solution. The amount of this correction is easily discovered, by determining the heat evolved during the solution of a corresponding weight of the dry compound in the normal proportion of water. If the combining bodies do not unite in more than one proportion, there only now remains to be determined the heat evolved or absorbed during the changes of aggregation which occur in the course of the combination. Unfortunately we cannot attempt, by direct experiments, to discover the amount of this important correction.

4. If we now make

$A =$  heat evolved during the reaction of chlorine, zinc (in excess), and water,

$B =$  heat evolved during the solution of  $ZnCl$  in a like proportion of water,

$X =$  heat evolved or absorbed during the change of the constituents

its oxide by means of hydrogen gas, although the action, as is well known, is most energetic if moisture be present. On the contrary, the dry gas instantly combines with arsenic, antimony, and phosphorus. This striking difference appears to depend upon the circumstance that the compounds formed by chlorine with the former substances are solid at common temperatures and very fixed, while those formed with antimony and arsenic are fluid and volatile. The chloride of phosphorus is also very volatile. If, however, the chemical affinity be very intense, combination will take place although the resulting compound be quite fixed and solid. Thus potassium inflames in dry chlorine gas, but the chloride which is formed terminates the action before the whole of the metal has entered into combination. The fluidity of the metal also exercises an important influence in determining the combination,—as in the case of mercury, which slowly combines with dry chlorine. The preceding remarks may be also applied to the behaviour of dry bromine when brought into contact with the metals.

of Zn Cl, from the state of aggregation in which they exist, as gaseous chlorine and metallic zinc, to that state in which they exist in the dry chloride of zinc,

$x$  = heat due to the union of zinc and chlorine,

we shall have the following general equation :

$$x = A - B \pm x.$$

And, designating the corresponding values for bromine by  $A'$ ,  $B'$ ,  $x'$ ,  $x'$ , and for iodine by  $A''$ ,  $B''$ ,  $x''$ ,  $x''$ , we shall have

$$x' = A' - B' \pm x',$$

$$x'' = A'' - B'' \pm x''.$$

5. The class of metals forming more than one compound with chlorine, bromine, and iodine is very numerous ; but none of them present the same facilities for this investigation as iron, to which accordingly I propose to confine my attention in the present paper. It is usually stated in chemical works that when chlorine, bromine, or iodine act upon an excess of iron filings, suspended in water, a solution of protochloride, protobromide, or protoiodide of iron is formed. But such a description gives a very imperfect idea of the successive series of phenomena which actually take place. We have only, indeed, to watch carefully the progress of the experiment, in order to discover that a sesquicompound ( $Fe_2Cl_3$ ,  $Fe_2Br_3$ ,  $Fe_2I_3$ ) is formed in the first instance, which afterwards, by combining with an additional atom of iron, becomes converted into the protocompound ( $Fe_2Cl_3 + Fe$ , &c.) To prove this, we only require to filter the liquid before the reaction has terminated, when a red solution will be obtained, having all the properties of a solution of a sesquisalt of iron, and yielding by evaporation a red deliquescent mass. Whether the experiment be made with chlorine, bromine, or iodine, the same results will be obtained. An elegant illustration of a similar train of changes is afforded by the action of chlorine gas on metallic tin. If we agitate an excess of tin filings with a little water in a glass vessel of chlorine gas, till the colour of the gas has scarcely disappeared, and instantly filter, the liquid which passes through will produce only a faint opalescence, when dropped into a solution of the bichloride of mercury ; but if the agitation be continued for only a few seconds after the disappearance of the chlorine, the filtered liquid will give a dense curdy precipitate when added to the same solution.

6. From these observations it follows, that the primary form of combination, into which the molecules of chlorine, bromine, and iodine enter with iron, is that represented by the formulas  $\text{Fe}_2\text{Cl}_3$ ,  $\text{Fe}_2\text{Br}_3$ ,  $\text{Fe}_2\text{I}_3$ , and that the so-called protocompounds are, in reality, secondary combinations, formed by the union of the sesquicom pounds with an additional atom of iron ( $\text{Fe}_2\text{Cl}_3 + \text{Fe}$ , &c.). This conclusion is farther confirmed by the well-known fact, that when these substances unite at elevated temperatures, the red or sesquicom pounds are always formed.\*

7. Let us now make

$c$  = heat evolved during the reaction of chlorine, iron (in excess), and water.

$d$  = heat evolved during the solution of  $\text{Fe}_2\text{Cl}_3$  in a similar proportion of water.

$e$  = heat evolved during the combination of  $\text{Fe}_2\text{Cl}_3$  in solution with Fe.

$y$  = heat evolved or absorbed during the change of aggregation of the constituents of  $\text{Fe}_2\text{Cl}_3$ .

$y$  = heat due to the union of  $\text{Fe}_2$  with  $\text{Cl}_3$ .

Let us also, as before, represent the corresponding values for bromine by  $c'$ ,  $d'$ ,  $e'$ ,  $y'$ , and for iodine by  $c''$ ,  $d''$ ,  $e''$ ,  $y''$ ,  $y''$ . The following equations will then give the values of  $y$ ,  $y'$ , and  $y''$ .

$$y = c - d - e \pm y,$$

$$y' = c' - d' - e' \pm y',$$

$$y'' = c'' - d'' - e'' \pm y''.$$

8. Having thus endeavoured to lay down general formulas for the heat of combination, I proceed to describe the experiments by which the values of  $a$ ,  $b$ ,  $c$ , &c. have been determined.

9. The apparatus employed in these experiments consisted of several distinct parts. The combination was effected in a thin glass vessel of the form represented in fig. 1. When chlorine was the subject of experiment, this vessel was

\* If the view, which regards  $\text{FeCl}$  as the primary form of combination, be preferred, it will be necessary to suppose that three successive changes occur,—first, the formation of the compound  $\text{Fe}_2 + \text{Cl}_2$ ; secondly, its conversion into  $\text{Fe}_2\text{Cl}_3$  by combining with  $\text{Cl}$ ; and thirdly, the reconversion of the latter into  $\text{Fe}_3\text{Cl}_5$  by its union with Fe.

filled with the gas in a moist state, and two very flimsy glass balls, such as those shown in fig. 4, were afterwards cautiously introduced. One of these balls contained a large excess of the metal in the state of fine filings ; the other, a quantity of water, whose weight had been adjusted nearly in the proportions before described. On the other hand, when bromine and iodine were under examination, the metal and water were introduced into the vessel itself, while the bromine, or iodine, carefully weighed, was contained in one of the little balls. The vessel was in all cases closed by a good cork, which was rendered air-tight by cement. A small stud of iron wire was inserted into the cork to maintain the glass vessel in its proper position in the interior of the apparatus. This vessel, thus prepared, was agitated for some time in water adjusted to the proper temperature, and then placed in the light copper vessel, fig. 2, which was immediately filled with water, and its lid screwed on. In the top and bottom of the copper vessel, loops of copper wire were inserted, by means of which it could be suspended, without contact of the hand, in the centre of a cylindrical vessel of tin plate, fig. 3, having a detached cover above and below. The complete arrangement will be readily understood from an inspection of fig. 5. In the lids of the tin cylinder and copper vessel corresponding apertures existed, through which the bulb of a delicate thermometer could be introduced into the water in the interior of the latter. On withdrawing the thermometer the aperture in the copper vessel could be closed, in the course of two or three seconds, without touching the vessel itself. By this arrangement the copper vessel with its contents was suspended in a fixed position in the centre of, but not in contact with, an outer cylinder of tin plate, while at the same time the temperature of the water could be noted at any time without removing it from its situation. A larger cylindrical vessel, capable of being rapidly rotated round its shorter axis, completed the whole apparatus. It is shown in fig. 6.

10. When an observation was made the copper vessel was suspended in the cylinder, the opening in its lid closed, and the apparatus placed in a horizontal position, and then cautiously agitated (lest the glass balls should break), till a perfectly uniform temperature was established through the whole of the copper vessel and its contents. This being accomplished, the cylinder was again placed in the position represented in fig. 5, the temperature of the water carefully noted, and the cork replaced. It was then suddenly shaken, so as to rupture the

glass balls within, and immediately afterwards secured in the interior of the larger cylinder, fig. 6, where the whole was rapidly rotated, for the space of five and a half minutes, from the time of observing the temperature. It was then removed, and the temperature of the water again observed. In the case of bromine and iodine, all that now remained to complete the experiment was to weigh the water in the copper vessel, but, in the case of chlorine, the original volume of the gas had to be determined. For this purpose, the glass vessel was placed in a water-trough, and the cork withdrawn. From the quantity of water which rushed in, the bulk of the chlorine was easily estimated. It is almost unnecessary to add, that, in every instance, the whole of the chlorine had entered into combination; the small residue being atmospheric air, unavoidably introduced when the bulbs were inserted.

11. The accuracy of experiments of this kind greatly depends upon the heat which is gained or lost by the apparatus during the course of the experiment. In a vessel placed apart from other sources of heat, the losses and gains of heat will evidently be equal to one another for equal differences of temperature above and below that of the surrounding air. But in the apparatus I have just described, from the proximity of the person of the observer, and the necessity of grasping the tin cylinder while placing it in, and removing it from, the rotating machine, this middle point is no longer the temperature of the air, but  $1^{\circ}.4$  above that point. Direct experiments also showed that the water had nearly attained its maximum point in  $45''$ , from the time when the glass balls were ruptured, and  $15''$  usually elapsed from the observation of the first temperature to the latter moment. We may, therefore, assume that the water is at the maximum temperature during  $4\frac{1}{2}'$ , and at the minimum during  $15''$ . If we put  $e$  for the excess of the final temperature above the air,  $e'$  for the difference between the initial temperature and the same, and  $r$  and  $r'$  for the corrections to be applied for the cooling and heating of the apparatus, during periods of  $4\frac{1}{2}'$  and  $15''$  respectively, we shall have

$$r = + (e - 1^{\circ}.4) \times 0.049,$$

$$r' = - (e + 1^{\circ}.4) \times 0.003 + 0^{\circ}.03.$$

12. The constant quantity  $0^{\circ}.03$  is added to the correction for simple heating, as an allowance for the heat, transmitted by the hand through the apparatus, while rupturing the balls. The temperature of the water being generally so ad-

justed, that the mean point between the initial and final temperatures was from half a degree to one degree above that of the air, the entire correction required was in all cases very small.

13. The value in water of the different parts of the apparatus was estimated with as much precision as possible. The specific heat of the copper and brass of the copper vessel was assumed to be 0.095, that of the glass of the glass vessel and balls was determined by a careful experiment to be 0.140. The leather, cork, and cement were found to be nearly equivalent to 1.1 gr. of water, and the specific heat of the solution formed in each experiment was also determined.

14. In the description of the experiments I have used the following abbreviations :

Bar.—The height of the barometer.

Th. air.—The temperature of the air.

$T^i$ .—The initial temperature of the water in the copper vessel.

$T^f$ .—The final temperature of the same.

Inc. c.—The increment of temperature corrected for heating and cooling, according to the formulas given before.

Aq.—The weight of the water in the copper vessel.

Sn.—The weight of water equivalent to the solution of the compound formed. This is found by multiplying the absolute weight of the solution by its specific heat, which is also given.

Vss.—The weight of water equivalent to the vessels and other solid substances used in each experiment.

15. The temperatures are given in the degrees of Fahrenheit's scale; the height of the barometer in English inches; the volume of the chlorine in cubic centimetres; and the weight of the water, &c. in grammes. The volume of the chlorine gas requires to be corrected for moisture, as well as for temperature and pressure, and I have assumed the weight of 100 cubic centimetres of the dry gas at 32°, and under a pressure of 29.92 in. to be 0.317 grammes.

#### COMPOUNDS OF ZINC.

16. Zinc and chlorine,  $Zn + Cl + Aq.$

Bar. . . . .	29.47	in. . . . .	29.07	in. . . . .	29.97	in.
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Th. air. . . . .	50°.70	. . . . .	48°.50	. . . . .	50°.80	
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T <sup>i</sup> .	47°.97	45°.22	49°.08
T <sup>f</sup> .	55°.20	52°.18	54°.14
Inc. c.	7°.34	7°.03	5°.12
Aq.	136.6 gm.	143.0 gm.	143.6 gm.
Sn. (sp. heat 0.76)	2.4	2.4	1.7
Vss.	21.3	21.3	21.3
Cl.	141.4 c. c.	141.0 c. c.	100.4 c. c.
Heat of comb.	2802°	2820°	2811°

Mean heat referred to chlorine as unit, 2811°.

Mean heat referred to zinc as unit, 3086°.

The first number indicates the number of degrees through which a portion of water, equal in weight to the chlorine, would be raised by the heat extricated during the combination; the second, the corresponding number of degrees for a portion of water equal in weight to the zinc.

17. Zinc and bromine, Zn + Br + Aq.

Th. air.	63°.40	64°.10	68°.3
T <sup>i</sup> .	61°.30	62°.07	66°.12
T <sup>f</sup> .	66°.94	66°.91	71°.12
Inc. c.	5°.70	4°.87	5°.03
Aq.	152.8 gm.	155.0 gm.	158.4 gm.
Sn. (sp. heat 0.62)	2.3	2.0	2.1
Vss.	19.4	19.4	19.4
Br.	0.936	0.806	0.847
Heat of comb.	1063°	1066°	1068°

Mean heat referred to bromine as unit, 1066°.

Mean heat referred to zinc as unit, 2586°.

18. Zinc and iodine, Zn + I + Aq.

Th. air.	64°.0	63°.80	38°.4
T <sup>i</sup> .	61°.08	60°.50	36°.74
T <sup>f</sup> .	66°.72	67°.67	42°.42
Inc. c.	5°.66	7°.24	5°.77
Aq.	159.5 gm.	161.1 gm.	129.1 gm.
Sn. (sp. heat 0.56)	3.8	4.9	3.2

Vss. . . . .	19.7	. . .	19.8	. . .	21.6
I. . . . .	2.372	. . .	3.084	. . .	2.000
Heat of comb. . .	436°.7	. . .	436°.2	. . .	444°.0

Mean heat referred to iodine as unit, 439°.

Mean heat referred to zinc as unit, 1720°.

19. To ascertain in the preceding cases the heat due to the solution of the compound, portions of each, carefully dried, were introduced into the thin glass balls, and the weight accurately ascertained, while the normal proportion of water for their solution was placed in the glass vessel.

20. Chloride of zinc and water, Zn Cl + Aq.

Th. air. . . . .	36°.90	. . .	37°.20		
T <sup>i</sup> . . . . .	35°.71	. . .	36°.05		
T <sup>f</sup> . . . . .	39°.00	. . .	38°.72		
Inc. c. . . . .	3°.29	. . .	2°.63		
Aq. . . . .	131.4 gm.	. . .	129.9 gm.		
Sn. (sp. heat 0.76)	10.6	. . .	8.4		
Vss. . . . .	21.7	. . .	21.7		
Zn Cl . . . . .	3.516	. . .	2.750		
Heat of comb. . . . .	292°	. . .	292°		

Mean heat referred to chlorine as unit, 292°.

Mean heat referred to zinc as unit, 320°.

21. Bromide of zinc and water, Zn Br + Aq.

Th. air. . . . .	54°.00	. . .	55°.50		
T <sup>i</sup> . . . . .	53°.86	. . .	55°.35		
T <sup>f</sup> . . . . .	56°.36	. . .	57°.41		
Inc. c. . . . .	2°.51	. . .	2°.06		
Aq. . . . .	153.9 gm.	. . .	154.9 gm.		
Sn. (sp. heat 0.62)	9.1	. . .	7.7		
Vss. . . . .	19.4	. . .	19.4		
Zn Br . . . . .	5.077	. . .	4.310		
Heat of comb. . . . .	127°	. . .	122°		

Mean heat referred to bromine as unit, 124°.5.

Mean heat referred to zinc as unit, 302°.

## 22. Iodide of zinc and water, Zn I + Aq.

Th. air.	. . . . .	58°.60	. .	59°.10	. .	38°.4
T <sup>i</sup> .	. . . . .	58°.02	. .	59°.12	. .	37°.58
T <sup>f</sup> .	. . . . .	59°.07	. .	60°.21	. .	40°.12
Inc. c.	. . . . .	1°.02	. .	1°.06	. .	2°.52
Aq.	. . . . .	159.1 gm.	. .	159.6 gm.	. .	125.6 gm.
Sn. (sp. heat 0.56)	. .	4.8	. .	5.0	. .	10.7
Vss.	. . . . .	19.1	. .	19.6	. .	21.6
Zn I	. . . . .	3.52	. .	3.92	. .	8.42
Heat of comb.	. . .	66°.5	. .	62°.6	. .	59°.3
Mean heat referred to iodine as unit,	62°.8.					
Mean heat referred to zinc as unit,	246°.					

## COMPOUNDS OF IRON.

23. Iron and chlorine, Fe<sub>2</sub> + Cl<sub>3</sub> + Aq + Fe.

Bar.	. . . . .	30.07 in.	. .	29.97 in.	. .	29.08
Th. air.	. . . . .	50°.50	. .	50°.50	. .	48°.00
T <sup>i</sup> .	. . . . .	47°.47	. .	47°.67	. .	45°.78
T <sup>f</sup> .	. . . . .	53°.78	. .	54°.08	. .	51°.93
Inc. c.	. . . . .	6°.36	. .	6°.47	. .	6°.23
Aq.	. . . . .	133.8 gm.	. .	143.9 gm.	. .	143.9 gm.
Sn. (sp. heat 0.74)	. .	2.2	. .	2.4	. .	2.4
Vss.	. . . . .	21.1	. .	21.3	. .	21.4
Cl.	. . . . .	131.7 c. c.	. .	141.5 c. c.	. .	141.5 c. c.
Heat of comb.	. . .	2503°	. .	2534°	. .	2505°
Mean heat referred to chlorine as unit,	2514°.					
Mean heat referred to iron in Fe <sub>2</sub> as unit,	4921°.					

24. It must be carefully observed that the unit here taken is not the whole of the iron dissolved, as in the case of zinc, but only two-thirds of it; because the remaining third does not enter directly into combination with the chlorine, as has been already explained.

25. Iron and bromine,  $\text{Fe}_2 + \text{Br}_3 + \text{Aq} + \text{Fe}$ .

Th. air. . . . .	64°.10	. . . . .	49°.00
T <sup>i</sup> . . . . .	61°.81	. . . . .	47°.52
T <sup>f</sup> . . . . .	66°.89	. . . . .	53°.55
Inc. c. . . . .	5°.10	. . . . .	6°.14
Aq. . . . .	155.3 gm.	. . . . .	147.4 gm.
Sn. (sp. heat 0.60)	2.4	. . . . .	2.7
Vss. . . . .	19.4	. . . . .	19.4
Br. . . . .	0.994	. . . . .	1.145
Heat of comb. . . . .	909°	. . . . .	909°

Mean heat referred to bromine as unit, 909°.

Mean heat referred to iron in  $\text{Fe}_2$  as unit, 3933°.26. Iron and iodine,  $\text{Fe}_2 + \text{I}_3 + \text{Aq} + \text{Fe}$ .

Th. air. . . . .	63°.40	. . . . .	63°.20	. . . . .	38°.10
T <sup>i</sup> . . . . .	61°.04	. . . . .	60°.30	. . . . .	36°.32
T <sup>f</sup> . . . . .	65°.99	. . . . .	65°.83	. . . . .	41°.44
Inc. c. . . . .	4°.97	. . . . .	5°.55	. . . . .	5°.17
Aq. . . . .	157.7 gm.	. . . . .	162.1 gm.	. . . . .	126.1 gm.
Sn. (sp. heat 0.54)	4.2	. . . . .	4.8	. . . . .	3.6
Vss. . . . .	19.6	. . . . .	19.5	. . . . .	21.6
I. . . . .	2.752	. . . . .	3.151	. . . . .	2.360
Heat of comb. . . . .	327°.8	. . . . .	328°.3	. . . . .	331°.5

Mean heat referred to iodine as unit, 329°.2.

Mean heat referred to iron in  $\text{Fe}_2$  as unit, 2299°.

27. The object of the experiments detailed in the three following tables was to determine the heat evolved, when solutions of the sesquichloride, sesqui-bromide, and sesquiiodide of iron are converted into solutions of the proto-compounds by agitation with an excess of iron. The sesquichloride of iron, obtained by the action of dry chlorine gas upon heated iron, was dissolved in water (the quantity being adjusted as usual) in the glass vessel, and an excess of iron filings was placed in one of the small balls. But I was obliged to have recourse to a different method in order to procure determinate quantities of the sesquibromide and sesquiiodide of iron in solution, from finding it impossible to

obtain these compounds in the dry state. At first I attempted to add an excess of bromine or iodine to solutions of known strength of the protocompounds; but, on endeavouring to expel the excess by heat, I found it difficult, even in the case of the sesquibromide of iron, to avoid the decomposition of the sesquicompound itself, when the solution was concentrated. The object in view was finally effected in a very complete and easy manner, by adding weighed quantities of bromine or iodine to solutions of the protobromide, or protoiodide of iron, containing more than twice as much bromine or iodine, as the quantity added. The object of employing a larger proportion of the proto-solutions than the bromine or iodine added would be capable of converting into the state of sesqui-compounds, was to prevent the possibility of any free bromine or iodine being present; and, as the results were the same, whether the excess of the proto-solution was greater or less, it evidently in no way interfered with the success of the experiment. In reducing the results we have, therefore, to remember that the sesquicompound formed, contains three times the quantity of bromine or iodine added, designated in the tables by  $\text{Br} \times 3$  and  $\text{I} \times 3$ .

28. Sesquichloride of iron and iron,  $\text{Fe}_2 \text{Cl}_3 \text{Aq} + \text{Fe}$ .

Th. air.	61°.80	62°.50	43°.00
T <sup>i</sup> .	61°.85	61°.35	41°.21
T <sup>f</sup> .	63°.34	64°.29	45°.45
Inc. c.	1°.46	2°.92	4°.25
Aq.	132.8 gm.	144.3 gm.	151.4 gm.
Sn. (sp. heat 0.73)	3.0	6.8	10.4
Vss.	21.8	21.4	19.9
$\text{Fe}_2 \text{Cl}_3$	0.856	1.895	2.900
Heat of comb.	406	402°	402°

Mean heat referred to chlorine in  $\text{Cl}_3$  as unit, 402°.5.

Mean heat referred to iron in  $\text{Fe}_2$  as unit, 788°.

29. Sesquibromide of iron and iron,  $\text{Fe}_2 \text{Br}_3 \text{Aq} + \text{Fe}$ .

Th. air.	44°.40	46°.70	47°.20
T <sup>i</sup> .	44°.46	46°.23	45°.77
T <sup>f</sup> .	46°.68	49°.02	50°.84
Inc. c.	2°.23	2°.81	5°.14

Aq. . . . .	152.6 gm.	152.4 gm.	152.1 gm.
Sn. (sp. heat 0.60) .	6.3 . .	7.3 . .	12.9
Vss. . . . .	19.6 . .	19.6 . .	19.6
Br $\times$ 3 . . . . .	2.163 . .	2.739 . .	5.199
Heat of comb. . . . .	184°.0 . .	183°.9 . .	182°.5

Mean heat referred to bromine in  $\text{Br}_3$  as unit, 183°.5.

Mean heat referred to iron in  $\text{Fe}_2$  as unit, 794°.

30. Sesquiiodide of iron and iron,  $\text{Fe}_2 \text{I}_3$  Aq + Fe.

Th. air. . . . .	47°.40 . .	47°.00 . .	51°.10
T <sup>i</sup> . . . . .	46°.41 . .	46°.87 . .	50°.15
T <sup>f</sup> . . . . .	49°.22 . .	49°.24 . .	54°.66
Inc. c. . . . .	2°.80 . .	2°.38 . .	4°.58
Aq. . . . .	151.2 gm. .	150.5 gm. .	146.8 gm.
Sn. (sp. heat 0.54)	9.1 . .	6.8 . .	17.7
Vss. . . . .	20.0 . .	19.9 . .	19.8
I $\times$ 3 . . . . .	4.497 . .	3.741 . .	7.596
Heat of comb. . . . .	112°.3 . .	112°.8 . .	111°.1

Mean heat referred to iodine in  $\text{I}_3$  as unit, 112°.1.

Mean heat referred to iron in  $\text{Fe}_2$  as unit, 783°.

31. To complete this part of the inquiry, it only remains to determine the heat evolved during the solution of the sesquichloride, sesquibromide, and sesquiiodide of iron in water. This I have been able to accomplish only in the case of the sesquichloride of iron, from having failed, as has been already remarked, in all my attempts to obtain the other two compounds in a dry state. Even a concentrated solution of the sesquibromide of iron allows bromine to escape during the process of evaporation. If the evaporation be carried to dryness, and the dry mass heated just to the point of fusion, a red substance remains, which is composed of one atom of the protobromide and one atom of the sesquibromide of iron ( $\text{Fe}_4 \text{Br}_5$ ). An approximation, however, may be made to the heat which would be developed during the solution of these compounds, by assuming that it will bear the same relation to the heat developed during the solution of the sesquichloride of iron, which has been already ascertained to exist in the case of the analogous compounds of zinc (20, 21, 22).

32. Sesquichloride of iron and water,  $\text{Fe}_2\text{Cl}_3 + \text{Aq.}$ 

Th. air.	60°.5	41°.4
T <sup>1</sup> .	60°.2	41°.02
T <sup>f</sup> .	61°.93	42°.10
Inc. c.	1°.68	1°.04
Aq.	132.8 gm.	120.4 gm.
Sn.	2.7	1.6
Vss.	21.7	19.3
$\text{Fe}_2\text{Cl}_3$	0.856	0.504
Heat of comb.	466°.	441°

Mean heat referred to chlorine in  $\text{Cl}_3$  as unit, 453°.Mean heat referred to iron in  $\text{Fe}_2$  as unit, 887°.

33. On the principle just stated, we may infer, as a rude approximation, that the heat disengaged during the solution of the sesquibromide of iron would be (referred to the iron as unit) 837°; and that disengaged during the solution of the sesquiiodide, 682°.

34. If we now substitute the numerical values, obtained by the preceding experiments, for the known quantities in the equations given before, we shall obtain

$$x = 3086^\circ - 320^\circ \pm x \quad (16, 20)$$

$$x' = 2586^\circ - 302^\circ \pm x' \quad (17, 21)$$

$$x'' = 1720^\circ - 246^\circ \pm x'' \quad (18, 22)$$

$$y = 4921^\circ - 887^\circ - 788^\circ \pm x \quad (23, 32, 28)$$

$$y' = 3933^\circ - 837^\circ - 794^\circ \pm x' \quad (25, 33, 29)$$

$$y'' = 2299^\circ - 682^\circ - 783^\circ \pm x'' \quad (26, 33, 30)$$

From these equations we deduce

$$x \text{ or } \text{Zn} + \text{Cl} = 2766^\circ \pm x$$

$$x' \text{ or } \text{Zn} + \text{Br} = 2284^\circ \pm x'$$

$$x'' \text{ or } \text{Zn} + \text{I} = 1474^\circ \pm x''$$

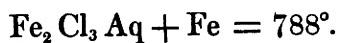
$$y \text{ or } \text{Fe}_2 + \text{Cl}_3 = 3246^\circ \pm x$$

$$y' \text{ or } \text{Fe}_2 + \text{Br}_3 = 2302^\circ \pm x'$$

$$y'' \text{ or } \text{Fe}_2 + \text{I}_3 = 834^\circ \pm x''$$

35. It must be remembered that each of the letters  $x$ ,  $x'$ , &c. represents two unknown quantities; first, the change of temperature due to the alteration of aggregation of the particles of the metallic elements, in passing from their ordinary form to that form in which they exist in the dry salt; and, secondly, the change of temperature arising from the like alteration of aggregation of the particles of the electro-negative element. The actual value of these quantities cannot be determined by direct experiments, but it is probable that for the combinations of the same metal, the differences between  $x$ ,  $x'$ , and  $x''$ , and between  $y$ ,  $y'$ , and  $y''$  will arise chiefly from the alterations of aggregation of the electro-negative, and not of the metallic element. Now, as the heat arising from the condensation of chlorine from the gaseous to what may perhaps be termed the saline solid state, must be far greater than that arising from the change of fluid bromine, or solid iodine, to the same state, it would be an object of great interest to determine the heat evolved or abstracted during the changes of these bodies from one physical condition to another, which would enable us to compare the heat of combination of each body in the same physical state. This I have only attempted yet to effect for the case of the solidification of bromine; and, as the result of a very imperfect experiment, it may be stated, that the heat evolved during the passage of that substance from the fluid to the solid state, would be sufficient to raise an equal weight of water through  $24^\circ$ . This amount of heat is evidently far too small to account for the differences observed in the values of  $x'$  and  $x''$ , and of  $y'$  and  $y''$ ; from which it follows, that bromine and iodine, in the same physical state, evolve very different quantities of heat when combining with the metals.

36. On comparing the numbers deduced from the foregoing experiments (28, 29, 30) for the heat developed during the conversion of the sesqui-compounds of iron into the corresponding proto-compounds, by combining with half as much iron as they already contain, the very interesting general principle results, that, referred to the combining iron as unit, the heat evolved in all these cases of combination is the same. In fact, we have



The slight differences between these numbers are fully within the limits of the unavoidable errors of experiment, and leave no doubt of the truth of the principle just enunciated.

37. On a future occasion I hope to have an opportunity of describing a more extended series of experiments now in progress, on the heat developed during the combination of other elements with chlorine, bromine, and iodine; and, till that opportunity occurs, I shall reserve any further observations of a general character upon the preceding results. Meanwhile they may be thus recapitulated:

1. The heat developed during the combination of a given quantity of zinc with chlorine gas is sufficient to raise an equal weight of water through 2766°, while that evolved during the combination of the same metal with bromine, in the fluid state, is 2284°; and with iodine, in the solid state, 1474°.

2. The heat developed during the combination of iron with chlorine, bromine, and iodine (which always takes place under the form  $\text{Fe}_2\text{Cl}_3$ ,  $\text{Fe}_2\text{Br}_3$ ,  $\text{Fe}_2\text{I}_3$ ) is sufficient to raise an equal weight of water through 3246°, 2302°, and 834° respectively.

3. When solutions of the sesquichloride, sesquibromide, and sesquiiodide of iron become converted into proto-compounds by combining with iron, the heat evolved in all is the same for the same quantity of iron dissolved.